Electronic Supplementary Information (ESI)

Polyoxometalate-based hybrid organogels prepared from a triblock copolymer via charge-driven assembly

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1. Synthesis and Characterization of Triblock Copolymer

Macro-initiator Br-EG$_n$-Br. The macro-initiator Br-EG$_n$-Br was synthesized by esterification reaction of poly(ethylene glycol) with 2-bromoisobutyryl bromide according to reference [1]. All poly(ethylene glycol) (PEG) samples used are from Fluka with molecular weight of 6,000, 10,000 and 20,000, corresponding to EG$_{136}$, EG$_{227}$ and EG$_{454}$.

Triblock copolymer 4VP$_m$-EG$_n$-4VP$_m$. The triblock copolymer 4VP$_m$-EG$_n$-4VP$_m$ was synthesized via atom transfer radical dispersion polymerization [2]. A typical procedure is as follows. 5 g of the macro-initiator Br-EG$_n$-Br ($M_{n,PEG}$ = 20,000), 12 mL of distilled water, 12 mL of ethanol, 72 mg of copper (I) bromide (Sigma Aldrich), 91 mg of *N,N,N',N'',N''*-pentamethyldiethylenetriamine (Sigma Aldrich) and 12 mL of 4-vinyl pyridine (Sigma Aldrich) were added to a round bottom flask with a magnetic stirrer. After three freeze-pump-thaw cycles, the flask was placed in an oil bath at 60 ˚C for 0.5 hours, and then the reaction mixture was extracted with chloroform. The extract was passed through a neutral alumina column to remove the copper, and after dry over magnesium sulphate, the triblock copolymer 4VP$_m$-EG$_n$-4VP$_m$ was isolated by precipitation in cold diethyl ether.

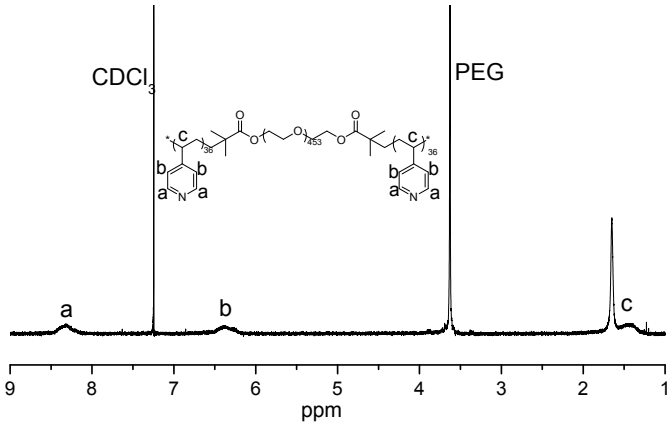

Figure S1 ^{1}H-NMR spectra of triblock copolymer 4VP$_m$-EG$_n$-4VP$_m$ in $CDCl_3$.

The triblock copolymer was dissolved in $CDCl_3$ to determine its structure by ^{1}H-NMR with a JEOL 270 MHz NMR spectrometer. Figure S1 presents the ^{1}H-NMR spectrum of 4VP$_m$-EG$_n$-4VP$_m$. The degree of polymerization (DP) for the P4VP block was calculated to be 36 from the ratio of the integrals of peaks **a**, **b** and **c** to the peak of PEG. Taking into account the amount of protons in a PEG monomer and groups **a, b** and **c** of the triblock copolymer**,** the DP was determined by $DP = \frac{4(I_a + I_b + I_c)}{7I_{PEG}} N_{PEG}$ with I_a, I_b and I_c representing the integral of peaks **a**, **b** and **c**, respectively; I_{PEG} is the integral of the PEG peak and N_{PEG} = 454 the degree of polymerization of the starting PEG. Based on the results, the triblock copolymer is 4VP$_{36}$-EG$_{454}$-4VP$_{36}$.

By the same methods, the structures of the other two triblock copolymers were calculated to be $4VP_{87}$-EG_{227}-$4VP_{87}$ and $4VP_{11}$-EG_{136}-$4VP_{11}$.

The gel permeation chromatography (GPC) was performed on a Shimadzu gel permeation chromatography system equipped with a Waters 1515 isocratic HPLC pump and a Wyatt technology optical DSP interferometric refractometer. *N,N*-dimethylformamide (DMF) was used as eluent at a flow rate of 1.0 mL/min, and poly(methyl methacrylate) was used to calibrate molecular weight and polydispersity index (PDI). The results are listed in Table S1, and it can be seen from the table that the molecular weights of $4VP_m$-EG_n-$4VP_m$ are larger than the corresponding macro-initiators Br-EG_n-Br, implying the synthesis of triblock copolymer.

Table S1 GPC results of macro-initiators Br-EG_n-Br and triblock copolymers $4VP_m$-EG_n-$4VP_m$

	Chemicals	M_n	PDI
1	Br-EG_{454}-Br	26,900	1.31
2	$4VP_{36}$-EG_{454}-$4VP_{36}$	79,300	2.59
3	Br-EG_{227}-Br	18,900	1.11
4	$4VP_{87}$-EG_{227}-$4VP_{87}$	57,300	2.75

2. SAXS Fitting

The measured SAXS scattering data were corrected for background scattering. The curve fittings were performed by using the SASfit program, which was downloaded from http://kur.web.psi.ch/sans1/SANSSoft/sasfit.html. DMF is a good solvent for both $4VP_{36}$-EG_{454}-$4VP_{36}$ and HPW, but after complexation, the P4VP blocks tend to form cores with the middle PEG blocks forming shell to stabilize the solvophobic cores, since DMF cannot dissolve the protonated P4VP blocks.

3. Movie

One short movie is available to demonstrate hybrid organogel formation: a typical process for organogel formation upon mixing $4VP_{36}$-EG_{454}-$4VP_{36}$ solution and HPW solution.

4. References

[1] K. Jankova, X. Chen, J. Kops, W. Batsberg, *Macromolecules* **1998**, *31*, 538-541.
[2] W.-M. Wan, C.-Y. Pan, *Macromolecules* **2007**, *40*, 8897-8905.